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To Mr. F.J. Kee
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SAMPLE PREPARATION PROCEDURES FOR LASER ENHANCED RADIOCARBON DATING

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Groundwater and other carbon containing materials up to 40,000 years old can be dated by measuring the Carbon 14 content of the sample. Older samples which contain less Carbon 14 (^{14}C) can be dated without degrading the quality of the measurement by using a laser to increase the $^{14}C/^{12}C$ ratio in the sample. This enrichment can also be used to improve the accuracy of younger samples and to reduce accelerator time per sample. Sample size requirements and possible sample preparation procedures are presented.

INTRODUCTION

In order to select suitable nuclear waste disposal sites, information on the history of water movement at potential sites is useful. One way of gaining information on the groundwater flow pattern is from carbon dating of water samples from the site. A research program has been undertaken as part of the Technical Assistance to AECL program to investigate the role that laser enrichment of Carbon-14 could play in the dating of such samples. This report examines sample preparation procedures connected with the use of laser enrichment in the dating process. It also examines the size of carbon samples that are required for dating when laser enrichment is used.

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BACKGROUND

Dating of carbon containing materials is based on the following principle. Carbon 14 (^{14}C) is the radioactive isotope of carbon with a 5730 year half life. Organic matter formed 5730 years ago will have only half as much ^{14}C as matter formed today. Organic matter formed 10 half lives ago (57300 years) contains $(\frac{1}{2})^{10}$ as much ^{14}C as matter formed today. Dating of material up to 40,000 years old is possible by counting the decay rate of the sample/1/. About 1 g of carbon is required for old samples using this technique. Accelerator-based mass spectrometers can date samples of similar age using samples as small as 200 µg/2/3/4/.

Samples as old as 75,000 years have been dated by increasing the $^{14}C/^{12}C$ ratio in the sample by a factor of 6/1/. Thermal diffusion was used as the enriching process. Enrichment takes five weeks with this process and sample sizes of 100 g are required. Electromagnetic isotope separation has also been used to enrich ^{14}C/4/. Although the $^{14}C/^{12}C$ ratio in samples has been increased by up to 500 with this technique, it is extremely wasteful of carbon sample. Substantial amounts of carbon 14 are lost due to (a) incomplete ionization, (b) scattering out of the collimated beam, and (c) losses at the ion collector. Sample handling losses of at least a factor of 100 exclusive of any losses associated with the enrichment process can be expected.

In any enrichment process, the $^{14}C/^{12}C$ ratio is enhanced by throwing away ^{12}C while retaining some or most of the ^{14}C. The sample size is reduced. Laser enrichment methods can increase the $^{14}C/^{12}C$ ratio by factors of up to 100 or more in a few hours making the dating of even older samples possible/5/6/. Sample preparation time will be substantially reduced when compared with thermal diffusion and sampling losses will be much lower than with electromagnetic separation. In the laser method, samples to be dated are converted to formaldehyde (CH_2O). Other molecules could be used for this laser enrichment step but formaldehyde was chosen because high enrichment factors have been demonstrated with this molecule/5/6/ and because it appears to be the easiest molecule to synthesize from carbon dioxide for which high laser driven carbon isotope enrichment factors have been demonstrated. An ultraviolet laser is tuned to a frequency which preferentially dissociates $^{14}CH_2O$ molecules producing carbon monoxide with a substantially higher $^{14}C/^{12}C$ ratio than in the original sample. In addition to allowing older samples to be dated, $^{14}C/^{12}C$ enrichment could also improve the accuracy of measurements on younger samples and reduce the accelerator counting time required per sample by bringing the $^{14}C/^{12}C$ ratio up to that of modern samples of organic matter.

SAMPLE PREPARATION FOR ACCELERATOR BASED MASS SPECTROMETERS

Small groundwater samples are usually dated by recovering the carbon dioxide contained in the carbonates dissolved in the water and converting the carbon dioxide to carbon/7/. Other carbon samples are generally also oxidized to carbon dioxide before processing. Although samples as small as 200 μg have been dated, carbon dioxide samples containing at least 1 mg of carbon are generally required for accurate dating. This limitation is imposed by the sample preparation procedure, not by the accelerator.

At the University of Toronto and the University of Rochester samples are converted to carbon by a multistep process which begins with reaction with lithium to form lithium carbide followed by reaction with water to form acetylene (C_2H_2). A radio frequency field is used to convert the acetylene to carbon/7/.

SAMPLE ENRICHMENT

Laser enrichment has not been applied to any carbon dating samples as yet. The main difficulty is handling very small samples without significant contamination or loss. Chemical conversion reactions of carbon dioxide have recently been reviewed/8/ to determine methods of converting ^{14}C containing carbon dioxide recovered from CANDU reactors into carbon monoxide for use in recovering the ^{14}C by cryogenic distillation or by laser enrichment/9/.

The lowest volume procedure appears to be to first convert the carbon dioxide (CO_2) to carbon monoxide (CO) by one of

(a) reaction with hot zinc/7/

$$CO_2 + Zn \rightarrow CO + ZnO$$

or

(b) reaction with carbon containing a very low level of ^{14}C (ie derived from oil or natural gas)

$$CO_2 + C \rightarrow 2CO$$

or

(c) reaction with hydrogen in the presence of a commercial zinc oxide/copper oxide catalyst

$$CO_2 + H_2 \rightarrow CO + H_2O$$

and then to convert the carbon monoxide (CO) to formaldehyde (CH_2O) by reaction with hydrogen

$$CO + H_2 \rightarrow CH_2O$$

This reaction is catalyzed by ultraviolet light from a mercury lamp. Mercury vapour must be present in the reaction cell. Oxygen-17 and Oxygen-18 containing formaldehydes have been synthesized with 80-90% yield by this technique/10/.

These sequences of reactions have not been performed together and the size of the apparatus to perform these reactions would have to be scaled down by a factor of 10 to 50 from what has been previously used. Sample preparation apparatus is described in Appendix A.

An experimental demonstration of this technique would be required before it can be used to prepare samples for carbon dating in order to:

1) Select the best method of converting from CO_2 to CO. (The reaction with zinc has been used in preparing samples for dating at the University of Seattle and may be the best candidate.)

2) Optimize experimental conditions of temperature, pressure, flow rates, etc.

3) Measure the efficiency and material losses associated with preparing carbon monoxide and formaldehyde.

4) Determine if there is any incompatibility with conditions required for the reaction producing carbon monoxide and the reaction producing formaldehyde.

5) Demonstrate that the apparatus can be scaled down sufficiently to handle the smallest amounts of carbon that can be handled by an accelerator based mass spectrometer.

SAMPLE SIZE

When the laser enrichment technique is used in the dating of a carbon sample, the minimum sample size, MSS, required, expressed in mg of carbon in the original carbon dioxide sample is a function of several factors. These include the minimum amount of carbon required by the accelerator-based mass spectrometer, S, the laser enrichment factor, EF, which is defined as the $(^{14}C/^{12}C)$ ratio in the laser dissociation products over the $(^{14}C/^{12}C)$ ratio in the starting material, the efficiency of conversion of carbon dioxide to carbon monoxide expressed as a fraction, E_{CO}, the efficiency of conversion of carbon monoxide to formaldehyde expressed as a fraction, E_{CH_2O}, the fraction of the ^{14}C-formaldehyde dissociated by the laser in the enrichment process, D, and the fractional loss of carbon due to handling, L.

$$MSS = \frac{EF}{E_{CO} \cdot E_{CH_2O} \cdot D \cdot (1-L)} \cdot S$$

Since the enrichment factor, EF, will never be less than 6 and using 1 mg for the minimum sample size, S, and assuming $E_{CO} = 0.99$, $E_{CH_2O} = 0.9$, D = 0.9 and 1-L = 0.9, the minimum amount of carbon required in the sample of carbon dioxide to be processed before dating is 8 mg (≈250 ml of carbon dioxide at a pressure of 50 torr or 6.7 kPa). Note that the dominant factors in this equation are the sample size required by the accelerator, the fraction of the ^{14}C-formaldehyde dissociated by the laser, and the enrichment factor. For large carbon 14 enrichment factors, much larger carbon dioxide samples are required.

SUMMARY

1. Carbon 14 dating methods for groundwater and for other materials that contain some carbon can be extended to older samples if the $^{14}C/^{12}C$ ratio in the sample is enhanced by an isotope enrichment process.

2. Carbon 14 enrichment on younger samples will reduce the accelerator counting time required and improve the accuracy of the dating measurement.

3. If a laser process is used for the enrichment, chemical conversion of the carbon dioxide sample to formaldehyde is required.

4. Procedures for carrying out this chemical conversion on the very low sample sizes anticipated for carbon dating are suggested. Some development and testing is required before these procedures can be used.

5. A formula for calculating the minimum amount of carbon dioxide sample required for dating when enrichment is used is given.

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APPENDIX A

Apparatus for Converting Carbon Dioxide Samples to Formaldehyde

The apparatus shown in Figure 1 is designed to convert ^{14}C containing samples of carbon dioxide to formaldehyde prior to laser enhancement of the ^{14}C to ^{12}C ratio. The apparatus is designed to handle small batch quantities of carbon dioxide.

A typical sample size for dating is about 250 mls of carbon dioxide at a pressure of 50 torr (6.7 kPa). The proposed, but as yet untested, conversion procedure involves the following steps:

1. The carbon dioxide sample container is connected to the apparatus.
2. The carbon dioxide to carbon monoxide conversion medium (zinc, carbon, or zinc oxide/copper oxide on alumina) is placed into the oven. The use of zinc will be assumed in future steps. Minor procedure modifications would be required with the other conversion medium.
3. The apparatus is pumped down to $\leq 10^{-4}$ torr by a vacuum pump.
4. The carbon dioxide sample is then distilled into the trap in the recirculation loop.
5. The carbon dioxide is recirculated over the hot zinc (about 450°C).
6. When the conversion to carbon monoxide is complete, (ie no carbon dioxide can be trapped in the liquid nitrogen trap in the recirculation loop) a large excess of hydrogen (3 to 6 times the amount of carbon dioxide in the original sample) is added to the loop.
7. If it proves necessary, the carbon dioxide to carbon monoxide conversion medium is valved out of the recirculation loop. The mercury lamp is turned on, and the drop of liquid mercury is exposed to the gas mixture.
8. A liquid nitrogen cooled trap collects the formaldehyde product but allows the unreacted hydrogen and carbon monoxide to pass. Recirculation is necessary to minimize carbon dioxide formation in the quartz reactor/10/. Several hours of recirculation may prove necessary in order to achieve 90% conversion of carbon dioxide to carbon monoxide.
9. The formaldehyde is then transfered to one of the fractionation traps and separated from its impurities (eg water, carbon dioxide and glyoxal) by the trap to trap distillation between a dry ice trap (-78°C) and a trap cooled by an n-pentane slush bath.
10. Finally, the purified formaldehyde is distilled to a storage/transfer tube which is maintained at liquid nitrogen temperature (-196°C).

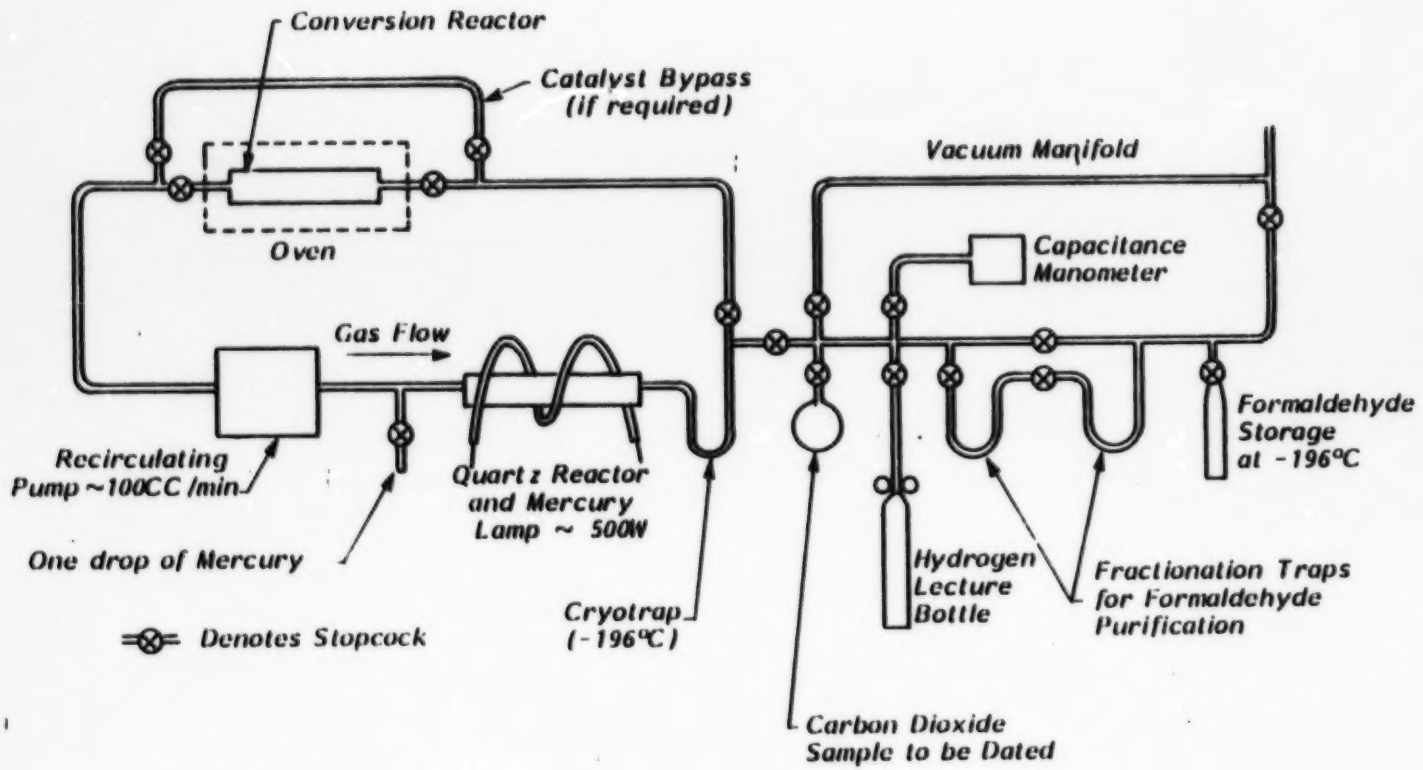

FIGURE 1

APPARATUS FOR CONVERTING CARBON DIOXIDE SAMPLES TO FORMALDEHYDE

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